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<https://doi.org/10.15017/12697>

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出版情報：九州大学農学部農場研究資料. 14, pp.40-43, 1992-03. University Farm, Kyushu University  
バージョン：  
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## A NEW ELECTROCHEMICAL METHOD FOR MEASUREMENT ORGANIC ACID CONTENT IN TROPICAL FRUITS BASED ON CONDUCTIVITY

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(International Symposium on Tropical Fruits, at PATTAYA, THAILAND, May 20-24, 1991 )

### Abstract

In order to estimate the quality of some tropical fruits, an attempt was made to apply the electrochemical measurement of the organic acid content in fruit juices. An equation (1) is set up between the content of organic acid in sample solution (y), and the specific conductance of the properly diluted solution (x). Where, the proportionality constant (a) is associated with nature of organic acids, closely relate to the dissociation constant of the acid,  $y = ax + b$  (1), and (b) is the constant due to the content of the strong electrolytes in sample solution.

### Introduction

Total acidity and sugars are important criteria of quality in tropical fruits, and Brix-acid ratio is an indication of the relative sweet- or sourness of fruits. A new rapid and convenient method was developed for measuring sourness of food based on conductometry.

Comparing the difference of the electrochemical behavior between weak electrolyte, organic acid, and strong one, KCl, it was found that the hydrogen ion concentration dissociated from organic acid could be accurately estimated in the presence of strong electrolyte ions.

An apparatus for measuring the organic acid content was designed and constructed. The apparatus was equipped with constant current unit. The importance signal measured was converted from analogue to digital and represented as acid content(%), after arithmetically computed with the corresponding equation. Compensation for the error resulted from the circuit was carried out automatically with the internal standard resistance at every measurement. The error of measurement was within 0.1 % as conductance value.

A special temperature correction method was developed by a combination of a standard potassium chloride solution and the temperature coefficient of organic acid. In using the method, the acid content could be determined at the temperature range 5~35 °C the deviation was less than 0.04 % as citric acid. The devised correction method was independent of the kind of organic acid, regardless of the variety of  $pK_1$ . The correction of the empirical errors, introduced by the measuring cell and contaminants in measuring water, and the check of reading would be simultaneously achieved by the temperature correction.

A design of conductance cell intended for practical determination of the organic acid content in food by means of the method based on cell conductometry is described. A simple dipping cell with bright platinum plates as electrodes was manufactured and characterized electrochemically. The estimated admittance and the reciprocal of solution resistance completely coincided for  $10^{-3}$  to  $10^{-4}$  potassium chloride and /or the 300 times diluted solutions prepared from the sample solution containing 0.3 to 2.5 % organic acid as citric acid. A linear relation was obtained between the conductance measured by the cell the organic acid content titrated with standard sodium hydroxide solution; correlation coefficient,  $r=0.998$  and standard deviation,  $S_{y.x}=0.045$ . A advanced cell was devised and the cell constant ( $\theta$ ) was  $1.221 \text{ cm}^{-1}$  in the range of  $10^{-4}$  N potassium chloride; hence, a 300 times diluted of 0.1 N potassium chloride was adopted as the standard solution for calibration. The response time of the advanced cell was nearly zero and there was no change of the measured value for 30 minutes successive run.

This paper proposes the application of the conductometric method developed by Osajima et al. to the estimation of the organic acid content in tropical fruits.

#### Materials and Method

Apparatus : Conductance measurement equipment. The conductance of tropical fruit juice was measured with ACILYZER model-5. The block diagram of ACILYZER is shown in Fig. 1. The bright platinum plates was used as electrodes.

Materials and reagents : Mango fruits, Indian black berry fruits and pineapple fruits were gathered from the fruit area near Dukka city in Bangladesh. After being extracted from each fruit, the juices were centrifuged (10,000 G, 20 min.) at 0 °C and stored at -20 °C. Organic weak bases, imidazole, were introduced into the electrochemical measurement of organic acid content in juices based on conductivity. One hundredth molar imidazole aqueous solution system was employed. The deionized water with less than  $5 \mu\text{Scm}^{-1}$  was used throughout.

Procedures : The free organic acid content was designated as the percentage of citric acid from the value by titration of the juices diluted to 1:15 with 0.1 N sodium hydroxide solution until pH 8.1 was reached. The conductance cell was maintained at 25 and 30 °C in a temperature controlled water bath. Tropical fruit juices were diluted 100 and 300 times with water containing 0.01 M imidazole, and the specific conductance was measured at 25 and 30 °C.

#### Result

1. Indian balack berry : The relation between specific conductance and free acid content in juices were shown Table 1. An equation is set up between the free acid content in Indian black berry juices(y), and the specific conductance of the properly diluted solution(x).

- (1) For the solution diluted 100 times at 25 °C,  $y(\%) = 0.0271 x - 3.2029$  ( $r = 0.9845$ ).
- (2) For the solution diluted 100 times at 30 °C,  $y(\%) = 0.0339 x - 4.3891$  ( $r = 0.9850$ ).
- (3) For the solution diluted 300 times at 25 °C,  $y(\%) = 0.0157 x - 0.4217$  ( $r = 0.9400$ ).
- (4) For the solution diluted 300 times at 30 °C,  $y(\%) = 0.0171 x - 0.7053$  ( $r = 0.9826$ ).

2. Pineapple : The relation between specific conductance and free acid content in juices was shown Table 2. An equation set up between the free acid content in pineapple juices (y), and the specific conductance of the properly diluted solution (x).

- (5) For the solution diluted 100 times at 25 °C,  $y(\%) = 0.0352 x - 4.4260$  ( $r = 0.9709$ ).
- (6) For the solution diluted 100 times at 30 °C,  $y(\%) = 0.0139 x - 0.1412$  ( $r = 0.9163$ ).
- (7) For the solution diluted 300 times at 25 °C,  $y(\%) = 0.0139 x - 0.2938$  ( $r = 0.9493$ ).
- (8) For the solution diluted 300 times at 30 °C,  $y(\%) = 0.0139 x - 0.2938$  ( $r = 0.9493$ ).

3. Mango : The relation between specific conductance and free acid content in juices was shown Table 3. An equation is set up between the free acid content in mango juices (y), and the specific conductance of the properly diluted solution (x).

- (9) For the solution diluted 100 times at 25 °C,  $y(\%) = 0.0224 x - 2.5969$  ( $r = 0.8016$ ).
- (10) For the solution diluted 100 times at 30 °C,  $y(\%) = 0.0381 x - 5.1633$  ( $r = 0.9153$ ).
- (11) For the solution diluted 300 times at 25 °C,  $y(\%) = 0.1439 x - 0.4994$  ( $r = 0.9196$ ).
- (12) For the solution diluted 300 times at 30 °C,  $y(\%) = 0.0162 x - 0.8092$  ( $r = 0.9734$ ).

#### Discussion

Relationship between specific conductance and free acid of this system are shown in Fig.2. The regression of free acid upon specific conductance indicated the highest correlation coefficient in case of the same species and the same dilution. And the regressions of tropical fruits juices were identical during the period of maturity fruits. It

was found to be able to determine the free acid content directly from the conductance by the use of the relationship of the titration value and the specific conductance of diluted tropical fruits juices without the influence of sugar and inorganic matters.

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Table 1. The free acid contents and specific conductance in Indian black berry juices diluted 100 and 300 times with water containing 0.01M imidazole at 25 and 30 °C.

Diluted time	100		300	
Temperature	25	30	25	30
(Free acid %)	(Specific conductance)			
1.045	156.7	161.1	95.1	105.9
0.948	154.8	158.9	84.8	95.4
1.051	154.8	158.8	90.1	99.3
1.035	155.6	158.3	91.2	101.3
0.547	137.3	144.9	60.9	70.5
0.427	134.7	142.6	59.4	69.6

Table 2. The free acid contents and specific conductance in pineapple juices diluted 100 and 300 times with water containing 0.01M imidazole at 25 and 30 °C.

Diluted time	100		300	
Temperature	25	30	25	30
(Free acid %)	(Specific conductance)			
1.178	155.8	159.6	90.3	101.4
0.594	137.1	142.8	58.6	68.0
1.318	156.1	159.8	102.3	106.7
0.891	146.8	151.2	72.1	82.9
0.951	148.8	153.0	79.1	88.3
1.202	156.9	160.0	98.4	110.3
1.161	156.8	160.4	95.9	108.8
1.178	157.3	160.8	98.6	112.2

Table 3. The free acid contents and specific conductance in mango juices diluted 100 and 300 times with water containing 0.01M imidazole at 25 and 30 °C.

Diluted time	100		300	
Temperature	25	30	25	30
(Free acid %)	(Specific conductance)			
0.349	97.8	142.5	55.2	65.1
0.350	142.1	146.9	66.6	79.7
1.385	165.4	168.3	125.7	138.0
0.451	139.1	145.5	60.5	71.7
0.167	128.5	138.6	50.1	61.3
1.312	164.6	167.4	125.0	136.9
1.222	160.0	163.5	105.9	116.8
0.454	143.5	157.8	101.0	84.4
0.844	153.3	157.6	90.3	96.2

	100		300	
	25	30	25	30
(Free acid %)	(Specific conductance)			
0.411	134.1	143.6	57.0	68.2
0.304	141.8	147.6	60.4	73.7
1.422	165.1	167.7	141.0	137.8
0.240	133.9	142.0	60.3	69.2
1.302	163.5	166.9	121.5	132.6
0.267	147.8	154.0	68.4	80.4
0.964	157.1	161.3	109.1	106.4
0.287	140.7	146.7	70.7	74.1
0.244	134.4	143.3	54.4	66.1

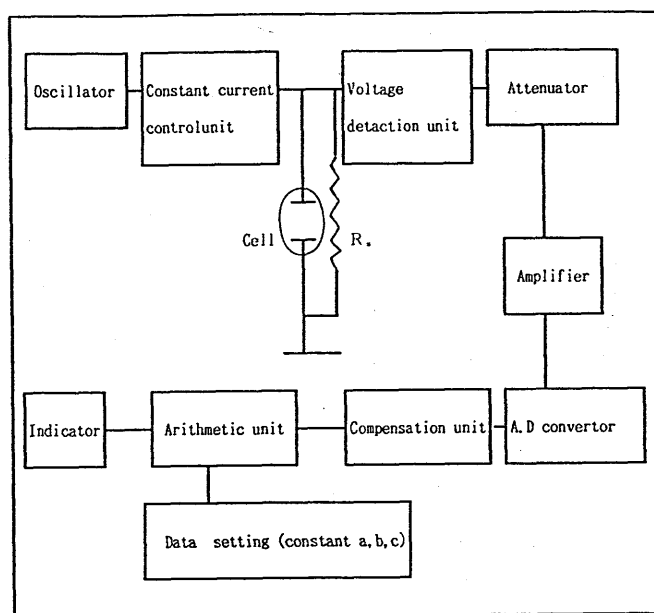


Fig. 1 Block diagram of ACYLYZER

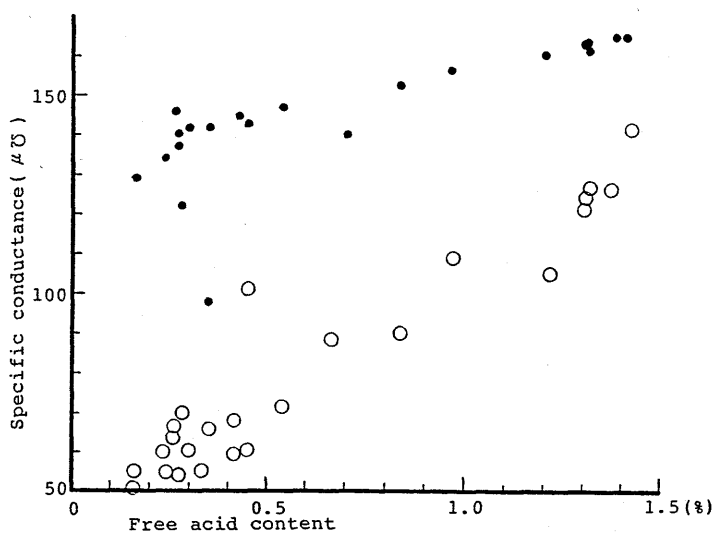


Fig. 2. Relationship between specific conductance and free acid of mango fruits.  
 ○: the solution diluted 100 times at 25°C.  
 ●: the solution diluted 300 times at 25°C.